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Two efficient processes for the synthesis of twelve, relatively water soluble, heterocyclium *closo*-dodecaborane $[B_{12}H_{12}]^{-2}$ and *closo*-dodecacarborane $[CB_{11}H_{12}]^{-1}$ salts by a one-step, open-air metathesis reaction have been developed. First, a combination of exhaustive trituration of the two solid reactant salts with refluxing anhydrous acetonitrile followed by flash filtration through a plug of silica gel affords excellent recovery for a broad series of otherwise water-soluble salts. Second, an alternative aqueous metathesis, driven to completion by precipitation of silver halides, followed by removal of water, re-dissolution in acetonitrile, and filtration through a plug of silica gel, affords complex heterocyclium borane salts albeit with possible minor "bleed-through" of the by-product KNO_3 salt. Mixed cation heterocyclium dodecaborane salts also can synthesized, and one example analyzed, shows melting point depression behavior.

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Pairing Heterocyclic Cations with *closo*-Icosahedral Borane and Carborane Anions. II. Benchtop Alternative Synthetic Methodologies for Binary Triazolium and Tetrazolium Salts with Significant Water Solubility (Preprint)

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Abstract: Two efficient processes for the synthesis of twelve, relatively water soluble, heterocyclium *closo*-dodecaborane $[B_{12}H_{12}]^{-2}$ and *closo*-dodecacarborane $[CB_{11}H_{12}]^{-1}$ salts by a one-step, open-air metathesis reaction have been developed. First, a combination of exhaustive trituration of the two solid reactant salts with refluxing anhydrous acetonitrile followed by flash filtration through a plug of silica gel affords excellent recovery for a broad series of otherwise water-soluble salts. Second, an alternative aqueous metathesis, driven to completion by precipitation of silver halides, followed by removal of water, re-dissolution in acetonitrile, and filtration through a plug of silica gel, affords complex heterocyclium borane salts albeit with possible minor "bleed-through" of the by-product KNO_3 salt. Mixed cation heterocyclium dodecaborane salts also can synthesized, and one example analyzed, shows melting point depression behavior.

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INTRODUCTION

In a previous publication,[1] a group of water-insoluble binary heterocyclium *closo*-icosahedral dodecaborane and dodecacarborane metathesized salts are obtained in excellent yields. These salts are generated using an open-air benchtop procedure conducted under aqueous conditions by combining stoichiometric quantities of potassium *closo*-dodecaborane or potassium *closo*-dodecacarborane with a variety of heterocyclium chloride, bromide, or iodide salts. The reactions are run by mixing the two metathesis component salts in hot deionized (DI) water followed by slow cooling in a refrigerator. These particular boron-based salt products are, as a group, very insoluble in water which permits trivial product salt isolation and efficient purification. These resulting heterocyclium *closo*-icosahedral borane and carborane salts are completely consistent with their instrumental characteristics (*i.e.*, NMR, IR, high resolution m/e, and/or single-crystal X-Ray) and are chemically free of any significant contamination by their associated by-product potassium halide precursor counter-ions. This latter issue was verified by direct analysis for [Cl]⁻ titer. Because many other new heterocyclium *closo*-icosahedral borane and carborane metathesis salts possess a high solubility in water, alternative synthesis methodologies are needed for their preparation. These process innovations are the subject of this work. Several other recent publications[2][3][4] also report the preparation of various solid salts that contain the *closo*-icosahedral carborane anion paired with a moderate selection of imidazolium cations and one pyridinium cation example.

RESULTS AND DISCUSSION

We sought a further generalization of this open-air benchtop metathesis methodology for synthesizing salts where additional triazolium cations, and new tetrazolium cations are paired

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with the *closo*-icosahedral borane and carborane anions (Scheme 1). In the pursuing this endeavor, we had to overcome at least two serious complications. First, when one attempts to
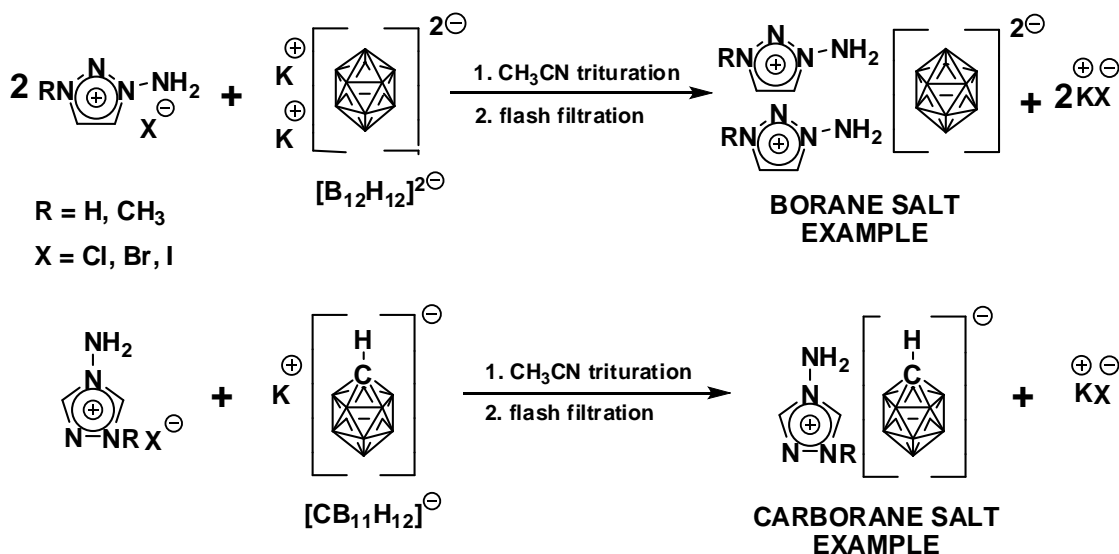
Scheme 1. Typical reactions of trituration-based metatheses.

perform a simple metathesis by combining 2.0 equivalents of [4-Amino-1-H-1,2,4-triazolium]Cl, with 1.0 equivalent of $K_2[B_{12}H_{12}]$ in warm DI water, instead of the desired adduct, a beautiful highly faceted crystalline solid deposits (Scheme 2) consisting of the pure [4-Amino-1-H-1,2,4-triazolium][K][$B_{12}H_{12}$] (**1**) salt product**.** The identity of this adduct was unambiguously
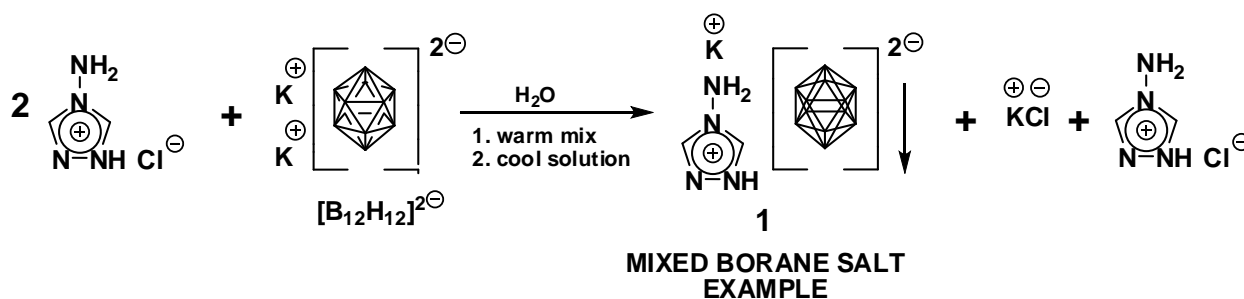
Scheme 2. Formation of the mixed mono-K/triazolium *closo*-borane salt (**1**).

ascertained by proton NMR integration and single crystal X-Ray crystallography[5] (Figure 1). Obviously, this result arises from the far lower solubility of the mixed mono-K/triazolium *closo*-icosahedral borane salt (**1**) compared to either starting materials **or** the desired metathesis salt
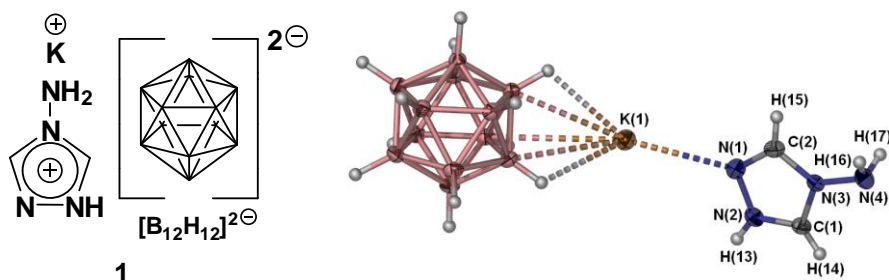

Figure 1. Graphical and molecular drawing of the mixed [4-amino-1,2,4-triazolium][potassium][*closo*-B$_{12}$H$_{12}$] salt (**1**) with thermal ellipsoids shown at 50% probability level.

product (**2**) as viewed in Scheme 2. The mono-K salt (**1**) insolubility precludes a direct water-driven metathesis for this example and necessitates developing an alternative methodology. Second, expansion of metathesis combinations that pair borane and carborane anions beyond previous imidazolium and triazolium examples[1] gave a variety of highly water soluble salts. For example, the metathesis reaction of [5-Amino-x-H-tetrazolium]Cl with either the borane, K$_2$[B$_{12}$H$_{12}$], or the carborane, K[CB$_{11}$H$_{12}$], reactants both lead to hydrated crystals of the desired product salts, (**4**) and (**5**), Figures 2 and 3, respectively, but because of their high water solubilities, only very low yields of the metathesis targets are recovered. Even highly concentrated aqueous solutions afforded only low yields of product. Thus, direct water-driven metathesis proved to be a highly inefficient process, especially given the expense of the commercial potassium *closo*-borane or potassium *closo*-carborane precursors. Development of

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an alternative non-aqueous methodology with a greater generality for water-soluble metathesis salt products became an important challenge.

Acetonitrile Trituration (Procedure A)

We investigated the combined use of exhaustive triturations with acetonitrile, followed by a flash filtration through silica gel (Scheme 1); and in doing so, we needed to ascertain the amount of KX that a given dry volume of silica gel would retain using a reasonable volume of eluting solvent. For KCl, 0.4473 g (6.0 mmoles) was partially solubilized in 100 mL of warm acetonitrile. After cooling to room temperature, the resulting turbid liquid was passed through 40 mL (dry volume) of silica gel, overlain with 20 mL (dry volume) of sea sand, and eluted with another 100 mL of acetonitrile. Less than 1 mg of residue was collected after solvent removal. For KNO_3, 0.6066 g (6.0 mmoles) was partially solubilized in 100 mL of warm acetonitrile. After cooling to room temperature, the resulting suspension was passed through 40 mL (dry volume) of silica gel, overlain with 20 mL (dry volume) of sea sand, and eluted with a further 100 mL of acetonitrile. Again, solvent removal afforded less than 1 mg of recovered residue.

In our metathesis process, once both solid salt reactants are mixed, our acetonitrile trituration/flash filtration approach is followed by careful removal of volatiles to give a series of finely divided amorphous powders. While many preliminary experiments were performed to seek a general re-crystallization solvent mixture for these powders, and while some individual successes resulted, we were unable to find such a general solvent system for efficient recrystallizations. So, rather than recrystallizing each individual adduct, we concentrated on performing a careful spectroscopic examination of the amorphous solids. This allowed us to directly compare the effectiveness of the trituration/filtration procedures across a group of

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reactants. We found that the isolated crude powders are indeed spectroscopically pure and have a moderately low content of [Cl]⁻ (Table I) in fair agreement with the above blank experiments done on a bolus of KCl suspended in acetonitrile. While a couple of values were higher than expected [Table I, salts (**4**) and (**5**)], further optimization with regards to number of triturations and trituration volume for particular substrates, might suffice to remove any excess chloride. Although we did not pursue this, a re-chromatography through an additional plug of silica gel might prove an effective means to reduce the halide concentration to miniscule values. [See the Experimental section for details on the [Cl]⁻ measurement procedure.]

TABLE I. Percent residual chloride ion content in synthesized salts (**2-11**).

Compound	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Percent Chloride by Weight	0.47	0.19	<u>3.06</u>	<u>2.41</u>	0.45	0.71	<udl[a]	0.30	<udl[a]	0.06
Percent Detection Limit	0.02	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.02	0.02

[a] "<udl" means "below detection limit"

This initial methodology exploits the significant solubility of many heterocyclium *closo*-icosahedral borane and carborane salts in boiling anhydrous acetonitrile versus the relative insolubility of the corresponding KCl by-product. The use of exhaustive trituration/plug

filtration works for a considerable variety of heterocyclium halide starting materials (see Experimental). We examined, via replicate experiments, reactions involving from 2-6 mmoles of the starting heterocyclium halide with no discernable variation in yield. For each preparative run, we performed a total of ten separate triturations and then pooled the triturant samples in a flask with cooling to room temperature prior to the flash filtration. In order to make the trituration process work at maximum efficiency and to minimize elution of the by-product KCl, it was found that the use of anhydrous acetonitrile was essential for successful flash filtration. HPLC-grade acetonitrile from Aldrich[®], used without any further purification and carefully protected via Parafilm™ after initially opening the bottle, was convenient. For this investigation, commercial silica gel of moderate sieve size (70-230 mesh; Merck[®]) was optimal. Semi-proportional scaling of the required silica gel from 22 mL (dry volume) to 40 mL (dry volume) and the additional eluting solvent volume from 80 mL to 120 mL were found satisfactory as the scale of reaction is increased from 2 to 6 mmoles, respectively. After evaporation of the trace acetonitrile remaining in the stirbar/recovery flask apparatus, a proton NMR (using DMSO-d6) performed on the residue indicated essentially complete removal of the starting metathesis reactant salts. When generalized to additional heterocyclium chloride examples beyond this paper, we suggest that such a trial NMR would indicate whether or not any further triturations are needed. This result could then be easily incorporated as feedback into a modified procedure. While heterocyclium iodides show significant solubility in acetonitrile, there may be instances where the amount of silica gel used does not scale to remove all the KI. This implies that a larger amount of silica gel might be needed for those runs. However, our experimental efforts with heterocyclium iodides focus on Procedure B (discussed later) where silver nitrate is employed to drive the metathesis to completion.

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Removal of the final traces of acetonitrile from the metathesis products is difficult.[6] A simple

azeotrope-type process was developed where a few mL of deionized water was added to the

sample followed by removal of all volatiles at high vacuum (final P ~ 40-50 mTorr). Occasional

modest heating of the flask with a heat gun, while under vacuum azeotrope conditions after water

addition, provided a process that was repeated three times. This effectively removed all the

residual acetonitrile. Incorporating this final solvent "distillation" into the overall process,

provided isolated yields of spectroscopically pure anhydrous metathesis product salts (**2-11**) as
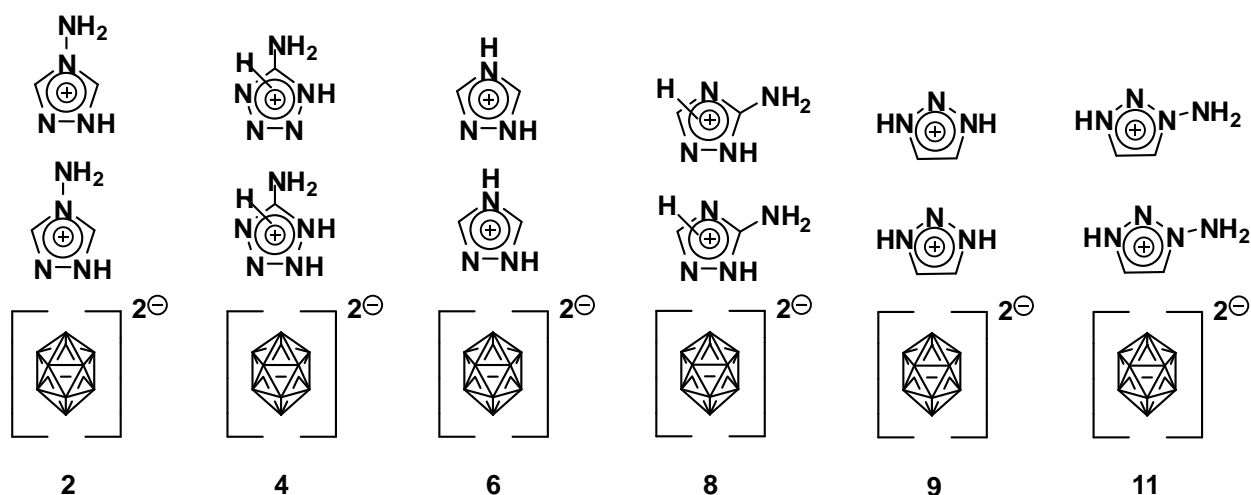

Figure 2. Binary [heterocyclium]$_2$[*closo*-B$_{12}$H$_{12}$] caborane salts synthesized.

finely divided amorphous solids in overall yields that ranged from 85-98% (Figure 2 and Figure

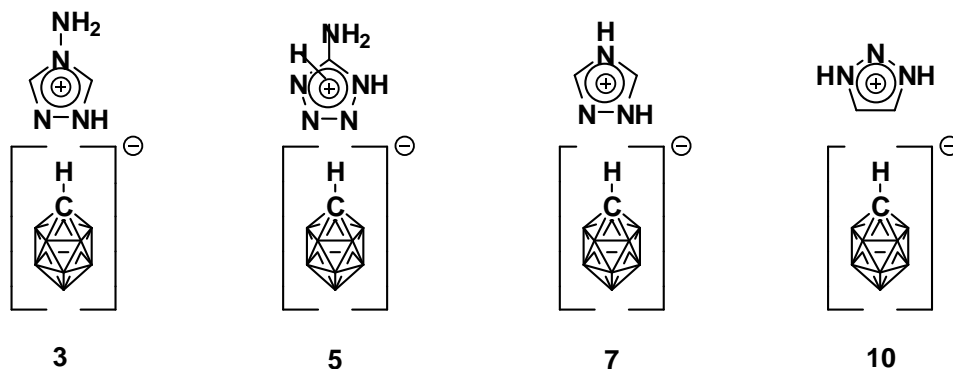3). For completeness, moderately water-insoluble examples from our earlier publication,[1] [4-

Figure 3. Binary [heterocyclium][*closo*-CB$_{11}$H$_{12}$] carborane salts synthesized.

Amino-1-H-1,2,4-triazolium][*closo*-CB$_{11}$H$_{12}$] (**3**) and [1-Amino-3-H-1,2,3-triazolium]$_2$[*closo*-B$_{12}$H$_{12}$] (**11**), were examined by Procedure A. The isolated flash-filtered products were obtained in high yields and with spectroscopic data identical to that previously reported.[1]

There is no significant difference in the results whether one employs either the potassium borane or potassium carborane as starting materials for this metathesis procedure. The starting boron-containing materials can be purchased from Katchem™ in the Czech Republic and are used without any further purification.[1]

Silver-Ion Driven Metathesis (Procedure B):

A second method for driving the metatheses reactions to completion uses a stoichiometric amount of aqueous silver nitrate to precipitate the halide gegenions as AgX. This process gives a mixture of several useful advantages and a possible disadvantage (see below). This procedure is particularly valuable in that the metathesis reaction is driven to completion by the extreme insolubility of the AgX. Furthermore, for borane salts, this process conveniently permits

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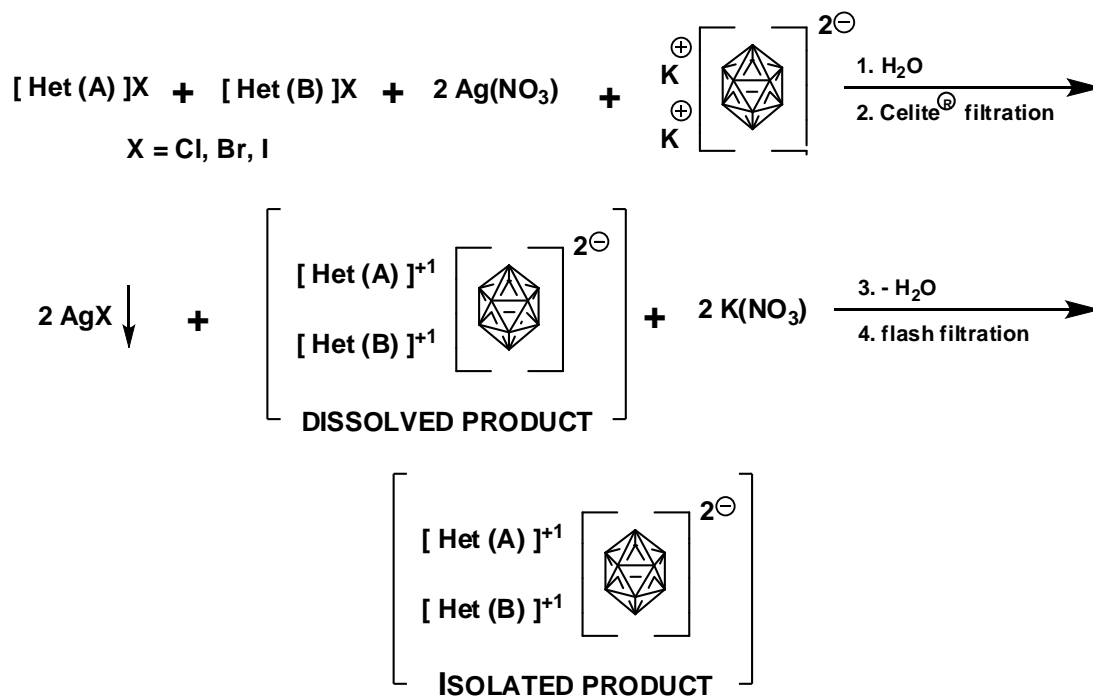
Scheme 3. Silver-ion driven metathesis and mixed borane salt capability.

reacting two different heterocyclium halides (simply by weighing them out separately) with potassium borane and using two equivalents of silver nitrate in water (Scheme 3) to yield mixed cation heterocyclium borane salts such as salt (**12**) seen in Figure 4. The immediate silver halide
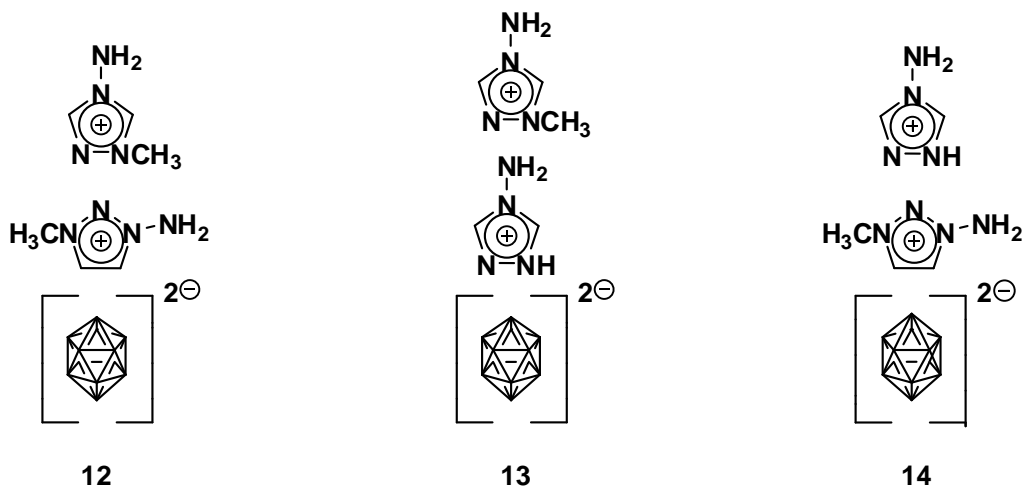

Figure 4. Mixed borane salts synthesized.

precipitate is filtered through a bed of moist Celite® affording a colorless aqueous filtrate that contains the desired product salt as well as two equivalents of KNO_3. Filtration of the aqueous solution from insoluble AgX, and removal of the water via a high vacuum line, gives a fluffy white powder. Dissolution of a small sample in DMSO-d6 affords a crude proton NMR spectrum that conforms **exactly** to the expected relative correct integrations of **all** key peaks. The initial mass balance is near theory when the presence of two equivalents of KNO_3 is included. Upon filtration of a re-suspension of the crude solid in acetonitrile through a plug of silica gel, overlain by sand, followed by removal of all volatiles (again, using the thrice "water azeotrope treatment"), an amorphous white solid is isolated that generally conforms to the expected proton and carbon NMR. In experiments involving the creation of a mixed heterocyclium borane salt (**12**) containing two different mono-cations (Figure 4), we initially were highly gratified to find that, after the plug filtration, this approach indeed gives the two heterocyclium ions in a precise 1:1 ratio based on NMR integrations of their distinctive peaks. However, **upon extremely careful analysis,** especially by comparing the integration of the very sharp N-methyl singlets (3H) to the borane B-H multiplet (12H), the borane integration is always slightly (*ca.*, 5%) higher than expected. Similar results were seen for the other mixed heterocyclium boranes (Figure 4). We are not certain what causes this anomaly but hypothesize that it probably results from "overloading" the adsorbent active sites on the silica gel with both the metathesis components as well as the KNO_3 by-product. Attempts to modify the elution, by taking smaller numbers of column volumes of elutant basically lowered the overall yield but did not improve this anomalous shortfall in the ratio of heterocyclium peak integrations versus the borane di-anion B-H integration. Nevertheless, within the caveat of the 5% integration anomaly, we were able to obtain moderately pure crude solids of various mixed heterocyclium salts with

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the desired borane di-anion. An alternative modification, use of a much higher relative amount of silica gel to substrates, was not employed since it would render this process far less convenient. We simply note these results and accept them as an inherent limitation of Procedure B.

The possible synthesis of "ternary"[7] mixed heterocyclium borane salts, which pair two different singly-charged heterocyclium cations with the borane di-anion (Figure 4), previously has been suggested.[1] While it is well-known that an admixture of two neutral compounds often affords eutectic behavior, we wondered whether or not the same phenomenology would result with salt mixtures. Perusal of the literature revealed a recent publication[8] in which three solid salts, when mixed together, gave a eutectic melt. This led to the supposition that a ternary mixed heterocyclium borane salt [such as (12)], with its two dissimilar heterocyclium cations, might possess a lower melting point, via an <u>intra-salt eutectic behavior</u>, than the melting points exhibited by two related binary salts [*e.g.* (15)[1] and (16).[1] Binary salts (15) and (16) each pair two identical heterocyclium cations with a borane di-anion, where the two cations of one salt [*e.g.* (15) <u>**or**</u> (16)] are the same as one of the dissimilar heterocyclium cations in borane salt (12). A melting point depression would also be expected, relative to each pure salt, when the two individual binary salts [(15) and (16)] are physically mixed in a mortar and pestle just prior to taking the melting point, thereby affording <u>inter-salt eutectic behavior</u>. Thus, <u>intra</u>-salt and <u>inter</u>-salt melting point behaviors are expected to be similar. Indeed, this is the case.

Preparation of the ternary mixed heterocyclium *closo*-borane salt (12) by the silver nitrate process (Procedure B) afforded a white solid with a crude, unrecrsytallized[9] m.p. of 136-142 ºC. When the two individual binary salts [each purified by recrystallization from DI water and having m.p., resp., 197-199 ºC[11] for (15) and 178-179 ºC[11] for (16)], were intimately mixed in

a 1:1 ratio by weight, the resulting admixture had a m.p. of 142-148 ºC (Figure 5). For completeness, a 2:1 ratio admixture gave a m.p. of 128-132 ºC and a 1:2 ratio gave a m.p. of 132-135 ºC. Thus, either gross mortar and pestle inter-salt mixing of individual binary heterocyclium salts (**15**) and (**16**), **or** an intimate intra-salt generation of the ternary mixed heterocyclium borane salt (**12**), via Procedure B, affords materials with relatively similar inter-salt and intra-salt eutectic melting points, respectively (Figure 5).

Weight Ratios/M.P. of 15:16

2:1   M.P. 128-132 ºC

1:1   M.P.142-148 ºC

1:2   M.P. 132-135 ºC

15
M.P. 197-199 ºC

16
M.P. 178-179 ºC

12
M.P. 136-142 ºC
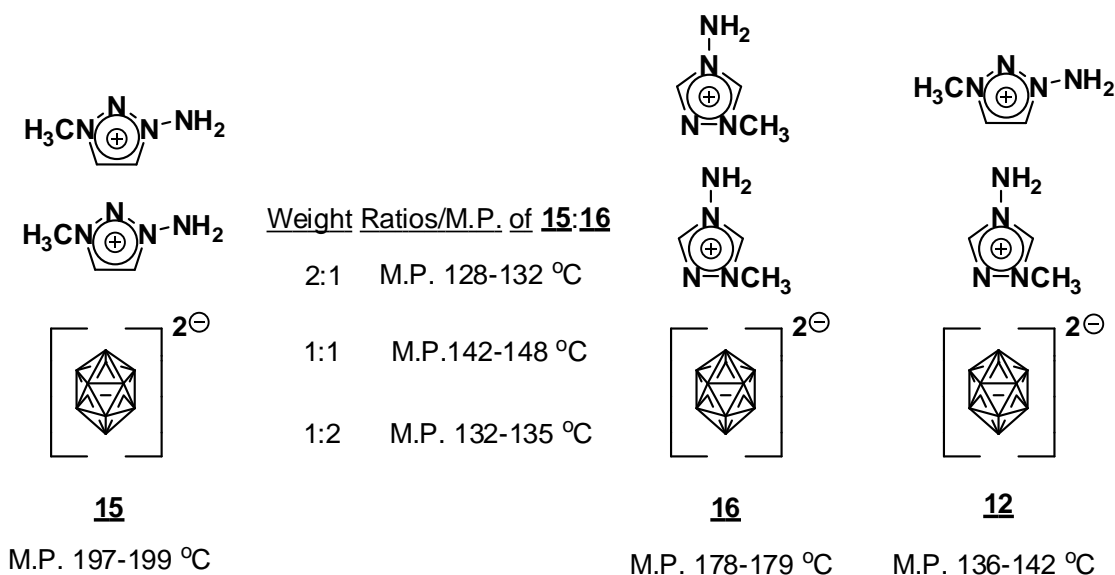
Figure 5. Inter-salt and intra-salt melting point depression comparison.

EXPERIMENTAL

General Comments. *Caution!* While no special precautions were taken in synthesizing and handling these borane-based salts, they are high energy materials and can be thermally,[12] impact, friction, and spark (ESD) initiated to rapid energy-releasing phenomena. Hazards testing was conducted on salts (**2**), (**4**), (**5**), and (**11**). Impact initiation testing determined the 100% value where no initiation occurs, and salt (**11**) was the most sensitive at 84 Kg-cm with salt (**5**) the least sensitive at 250 Kg-cm. For comparison, the following more sensitive Kg-cm values where 50% initiation results for known explosives is given: CL-20 at 33; PETN at 67; HMX at

115 and RDX at 117. Salt (**2**) was most sensitive to friction initiation at 14.4 Kg-cm, and salts

(**4**) and (**5**) were the least friction sensitive at 21.6 Kg-cm. Salt (**2**) also was the most sensitive to

spark initiation (ESD test) at 0.0025 Joule, and salt (**5**) was the least ESD sensitive at 1.00 Joule.

All neutral heterocycles that were converted to the hydrochloride (aq. conc. HCl followed

by recrystallization from EtOH/Et$_2$O) or the methiodide (CH$_3$I followed by recrystallization from

EtOH/Et$_2$O) were purchased commercially with only one exception. The 1-amino-1,2,3-triazole

was synthesized as described in the literature.[10] Deionized (DI) water was obtained from an in-

house Millipore MILL-Q Reagent Grade Water System™ at an 18 megaohm cm purity level.

All organic solvents were commercially purchased and were either Reagent Grade or HPLC-

purity. Most importantly, the acetonitrile used in the triturations and flash filtrations was HPLC-

grade, and the solvent container was carefully re-Parafilmed™ after each use to minimize any

accumulated moisture. **NMR Data:** A Brüker Avance™ 400 Digital NMR instrument was used

to obtain both proton (^{1}H) and carbon (^{13}C) spectra. Because this project is primarily one

involving process chemistry, we used commercial samples of Katchem™ K$_2$[B$_{12}$H$_{12}$] that

contain a small amount of [NHEt$_3$]$_2$[B$_{12}$H$_{12}$] as an impurity. By direct proton integration against

the main component, this impurity is approx. 1.5%.   One component of this impurity peak

overlaps with the B-H multiplet. Its integration contribution was negated (by simple subtraction)

from the (B-H) integrations for each new metathesized salt. However, this [NHEt$_3$]$_2$[B$_{12}$H$_{12}$]

"impurity" provided a constant "marker" for our reaction mixtures since the product salts were

not recrystallized. The sole exception to this for the salts (**1-14**) is (**1**) which was recrystallized

in water solvent. This completely removed the [NHEt$_3$][B$_{12}$H$_{12}$] impurity. **FTIR Data:** Fourier

transform infrared spectra (FTIR) were taken on powdered samples using a Nicolet 6700

Spectrometer™ in air with an HATR optical system. **Melting Point Data:** Commercial **Opti-**

Melt™ apparatus was used with video playback software. For typical acetonitrile-trituration runs, the isolated amorphous solids were not subjected to a melting point determination. **X-Ray Analysis:** Please refer to footnote number 5. **[Chloride]⁻ Ion Chromatography Data Collection:** Ionic Concentration was determined by Ion Chromatography using a Waters HPLC equipped with a Waters 432 conductivity detector and a Phenomenex™ STAR-ION™ A300 100 x 4.3 mm ID (PEEK™) column. A borate/gluconate eluent was used and system conditions were set according to Waters method #980895. Each salt sample was weighed between 0.01 mg to 0.05 mg in a plastic class B centrifuge tube and diluted to 25 mL using Type I ultra-pure water. Samples that did not readily dissolve were heated to 80°C with a plastic centrifuge cap. Each sample was passed through an IC Millex LG 0.2 μm syringe filter prior to injection. A 3-point calibration curve was generated using a blank, a 1 ppm, and a 10 ppm NIST traceable chloride standard. Concentrations were determined by comparing peak area response of the samples to the standard calibration curve.

Procedure A Synthesis: [General Procedure.] After weighing out the corresponding stoichiometric quantities of the heterocyclium halide salt and the appropriate potassium carborane or potassium borane salt, the solids are placed in a recovery flask equipped with a stirbar (flask and stirbar are tared together) and a Vigreaux reflux tube. Addition of pure acetonitrile (HPLC-grade only) is followed by placing the apparatus in a hot oil bath (internal T = 161-165 ºC}. After the contents of the flask reach a vigorous reflux, the suspension is then cooled to near room temperature and the supernatant is carefully transferred to an Erlenmeyer flask. Exhaustive trituration that was repeated 10 times, using an empirically derived volume of acetonitrile (10 mL for a 6 mmol scale and 6 mL for a 2-3 mmol scale of carborane or borane), results in complete removal of the reactive species while most of the by-product potassium

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halide remains in the original recovery flask. After cooling to room temperature, the combined triturated solutions in the Erlenmeyer flask are poured over an acetonitrile-moistened bed of 35 mL (dry volume) of silica gel and 8 mL (dry volume) of washed sea sand packed in a 125 mL coarse frit glass filter. An additional 100 mL of acetonitrile is passed through the adsorbent bed. The combined solvent is then rotovapped to dryness. To remove the last traces of acetonitrile, addition of 2 mL of DI water is followed by pumping at high vacuum, with periodic heat gun treatment, thereby affording a solid residue. This "semi-azeotrope" treatment is repeated a total of three times. This affords a clean white amorphous powder whose proton NMR integration is excellent, whose [halide]$^-$ weight percent is generally small (Table I),[11] and whose yields are acceptable. Individual samples were not recrystallized because each product required considerable experimentation to find a suitable single or mixed optimal solvent combination for recrystallization.

Procedure B Synthesis: [This general procedure has been adapted for a mixed cation system and is based on the reaction used to prepare **[4-Amino-1-Me-1,2,4-triazolium][1-Amino-3-Me-1,2,3-triazolium][*closo*-B$_{12}$H$_{12}$] (12).** The crystalline iodide [4-Amino-1-Me-1,2,4-Triazolium]I; 0.6781 g; 3.00 mmol), the crystalline iodide [1-Amino-3-Me-1,2,3-triazolium]I; 0.6781 g; 3.00 mmol), the borane K$_2$[B$_{12}$H$_{12}$]; 0.6601 g; 3.00 mmol), and the silver nitrate (1.0192 g; 6.00 mmol) were carefully weighed out separately and each was transferred separately to four different 50 mL beakers. To each of the beakers was added 4.0 mL of DI water, and the contents were warmed on a hot plate. Slowly, in the above order, the contents of the first three beakers were transferred to the fourth beaker and each of the first three beakers was rinsed with 2.0 mL of DI water. The resulting combined grayish suspension was stirred with a glass rod and then filtered through a pre-prepared moist bed of Celite®. The beakers were rinsed with a final 5

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mL of DI water. The filtrate was placed in a tared recovery flask and pumped for 40 hours on a high vacuum line (final P ~ 35 mTorr). The contents of the recovery flask were swirled with 70 mL of hot anhydrous acetonitrile, cooled to RT, and poured through a 125 mL (coarse frit) glass funnel with a pre-equilibrated (acetonitrile) bed of silica gel (38 mL dry volume) and overlain with sea sand (10 mL dry volume). Elution with a total of 200 mL of anhydrous acetonitrile was followed by removal of solvent (rotovap and high vacuum line). To the crude residue was added 3 mL of DI water, and the contents were heated repeatedly with a heat gun, while the volatiles were slowly removed under high vacuum. This process was repeated a total of three times to afford an off-white amorphous solid (0.9253 g; spectroscopically pure residue; see (**12**) (below) for spectroscopic details).

[4-Amino-1-H-1,2,4-triazolium][K)][*closo*-B$_{12}$H$_{12}$] (1): From 2.410 g (20.0 mmol) of [4-Amino-1-H-1,2,4-triazolium]Cl and 2.2003 g (10.0 mmol) of K$_2$[B$_{12}$H$_{12}$] in 11.0 mL DI water held at reflux for 10 minutes and cooled to 4 ºC overnight, there was isolated 1.3754 g (51.7%) of massive distorted rhombs (m.p. 207.2ºC (softening), 252.3-254.9ºC liquification with rapid gas evolution). This product was subjected to single crystal X-Ray crystallography[5]. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 9.47 (s, 2H), ~8.6 (br exchangeable peak 3H), 1.7-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 144.03. FTIR (HATR Method; significant peaks) 3318, 3226, 3145, 3109, 3061, 3036, 2479, 2461, 2435, 1747, 1733, 1623, 1546, 1524, 1425, 1360, 1334, 1202, 1070, 1034, 979, 946, 880 cm.$^{-1}$

[4-Amino-1-H-1,2,4-triazolium]$_2$[*closo*-B$_{12}$H$_{12}$] (2):. Yields: **Proc. A** = 85.8%; **Proc. B** = 91.7%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 9.43 (s, 4H), ~7.95 (br exchangeable peak, 6H), 1.9-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6

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center peak = 39.51) δ 144.05. FTIR (HATR Method; significant peaks) 3322, 3305, 3224, 3113, 2464, 2439, 1622, 1552, 1520, 1422, 1356, 1328, 1302, 1205, 1152, 1062, 1029, 976, 939, 870, 711, 682, 612, 576 cm.[-1]

[4-Amino-1-H-1,2,4-triazolium][*closo*-CB$_{11}$H$_{12}$] (3): [1] Yield: **Proc. A** = 93.7%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 9.49 (s, 2H), ~7.95 (br exchangeable peak, 3H), 2.38 (br s, 1H), 2.3-0.7 (complex multiplet, 11H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 144.03, 50.75. FTIR (HATR Method; significant peaks) 3612, 3346, 3285, 3126, 3052, 3023, 3003, 2929, 2514, 1634, 1610, 1512, 1422, 1352, 1319, 1201, 1144, 1094, 1062, 1025, 939, 919, 874, 711, 612 cm.[-1]

[5-Amino-x-H-tetrazolium]$_2$[*closo*-B$_{12}$H$_{12}$] (4): Yield: **Proc. A** = 98.4%; **Proc. B** = 96.5%). ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ ~8.16 (br exchangeable peak, 8H), 1.7-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 156.22. FTIR (HATR Method; significant peaks) 3559, 3497, 3403, 3330, 3199, 2480, 1699, 1634, 1581, 1442, 1409, 1311, 1258, 1140, 1066, 1046, 1001, 911, 774, 735, 715, 682, 625 cm.[-1]

[5-Amino-x-H-tetrazolium][*closo*-CB$_{11}$H$_{12}$] (5): Yields: **Proc. A** = 94.3%. **Proc. B** = 96.8%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ ~7.13 (br exchangeable peak, 4H), 2.38 (br s, 1H), 2.2-0.6 complex multiplet, 11H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 155.89, 50.73. FTIR (HATR Method; significant peaks) 3608, 3534, 3444, 3346, 3318, 3056, 2533, 1708, 1642, 1605, 1450, 1438, 1381, 1278, 1127, 1091, 1058, 1029, 760, 715, 666, 592, 559 cm.[-1]

[1-H-4-H-1,2,4-triazolium]$_2$[*closo*-B$_{12}$H$_{12}$] (6): Yield: **Proc. A** = 94.7%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ ~13.19 (br exchangeable peak, 4H), 9.22 (s, 4H), 1.7-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 143.54.

FTIR (HATR Method; significant peaks) 3438, 3297, 3278, 3252, 3225, 3126, 3058, 3020, 2461, 1644, 1557, 1523, 1398, 1264, 1143, 1063, 1033, 949, 877, 714, 653 cm.$^{-1}$

[1-H-4-H-1,2,4-triazolium][*closo*-CB$_{11}$H$_{12}$] (7): Yield: **Proc. A** = 94.7%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ ~12.52 (br exchangeable peak, 2H), 9.23 (s, 2H), 2.37 (br s, 1H), 2.3-0.7 (complex multiplet, 11H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 144.06, 50.72. FTIR (HATR Method; significant peaks) 3469, 3367, 3281, 3130, 3028, 2517, 1740, 1556, 1520, 1418, 1352, 1172, 1152, 1086, 1025, 886, 866, 711, 620 cm.$^{-1}$

[3-Amino-1-H-x-H-1,2,4-triazolium]$_2$[*closo*-B$_{12}$H$_{12}$] (8): Yield.: **Proc. A** = 90.1%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ ~13.37 (br exchangeable peak, 4H), 8.30 (s, 2H), ~7.99 (br exchangeable peak, 4H), 1.8-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 150.90, 139.48. FTIR (HATR Method; significant peaks) 3379, 3309, 3260, 3183, 3154, 3113, 2464, 1695, 1610, 1593, 1573, 1389, 1340, 1258, 1066, 1033, 952, 866, 715, 645, 604, 564 cm.$^{-1}$

[1-H-3-H-1,2,3-triazolium]$_2$[*closo*-B$_{12}$H$_{12}$] (9): Yield: **Proc. A** = 90.7%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 13.26 (br s, 4H), 7.96 (s, 4H), 1.7-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 130.35. FTIR (HATR Method; significant peaks) 3220, 3154, 3134, 3060, 3044, 2999, 2460, 1560, 1454, 1409, 1368, 1287, 1242, 1127, 1074, 968, 833, 776, 764, 715, 670 cm^{1}.

[1-H-3-H-1,2,3-triazolium][*closo*-CB$_{11}$H$_{12}$] (10): Yield: **Proc. A** = 96.2%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 12.44 (br s, 2H), 7.96 (s, 2H), 2.38 (br s, 1H), 2.3-0.7 (complex multiplet, 11H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 130.30, 50.79. FTIR (HATR Method; significant peaks) 3604, 3362, 3240, 3158, 3136, 3051, 3001,

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2951, 2905, 2516, 1946, 1854, 1657, 1611, 1553, 1503, 1453, 1407, 1357, 1230, 1118, 1091, 1068, 1022, 960, 883, 795, 760, 710, 671, 621 cm.$^{-1}$

[1-Amino-3-H-1,2,3-triazolium]$_2$[*closo*-B$_{12}$H$_{12}$] (11): [1] Yield: **Proc. A** = 96.7%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 8.41 (extremely br s, 6H), 7.942 (d, J = 0.8 Hz, 2H), 7.715 (d, J = 0.8 Hz, 2H), 1.7-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 132.10, 124.19. FTIR (HATR Method; significant peaks) 3301, 3224, 3187, 3154, 3126, 2484, 2451, 1593, 1544, 1466, 1401, 1295, 1168, 1148, 1107, 1074, 1058, 1021, 992, 944, 886, 792, 727, 656 cm.$^{-1}$

[4-Amino-1-Me-1,2,4-triazolium][1-Amino-3-Me-1,2,3-triazolium][*closo*-B$_{12}$H$_{12}$] (12): Yield: **Proc. B** = 90.8%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 10.04 (s, 1H), 9.15 (s, 1H), 8.730 (d, J = 1.2 Hz, 1H), 8.597 (d, J = 1.2 Hz, 1H), 8.25 (s, 2H), 6.92 (s, 2H), 4.22 (s, 3H), 4.03 (s, 3H), 1.7-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 145.02, 142.91, 131.51, 126.85, partially resolved N-CH$_3$ peaks on the DMSO-d6 carbon heptet − 39.75 vs. 39.71 and 38.92 vs. 38.88. FTIR (HATR Method; significant peaks) 3628, 3555, 3326, 3301, 3248, 3220, 3117, 3097, 3076, 2464, 2018, 1765, 1712, 1638, 1605, 1573, 1532, 1479, 1434, 1401, 1381, 1315, 1209, 1172, 1062, 960, 866, 796, 715, 657, 608 cm.$^{-1}$

[4-Amino-1-Me-1,2,4-triazolium][4-Amino-1-H-1,2,4-triazolium][*closo*-B$_{12}$H$_{12}$] (13): Yield: **Proc. B** = 81.2%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 10.04 (s, 1H), 9.44 (s, 2H), two overlapping singlets with essentially the same chemical shift), 9.14 (s, 1H), 7.00 (extremely br s, 5H), 4.03 (s, 3H), 1.8-0.0 (complex multiplet, 12H). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 145.06, 144.05, 142.95, and 38.97. FTIR (HATR Method; significant peaks) 3739, 3583, 3563, 3542, 3506, 3318, 3228, 3109, 3064, 3036, 2942, 2901,

2476, 1748, 1732, 1618, 1556, 1520, 1425, 1324, 1262, 1205, 1168, 1058, 1033, 980, 939, 886, 866, 754, 711, 678, 653, 612, 555 cm.$^{-1}$

[4-Amino-1-H-1,2,4-triazolium][1-Amino-3-Me-1,2,3-triazolium][*closo*-B$_{12}$H$_{12}$] (14): Yield: **Proc. B** = 71.7%. ^{1}H NMR (400.132 MHz, DMSO-d6 (center peak = 2.50) δ 9.44 (s, 2H), 8.728 (d, J = 1.2 Hz, 1H), 8.595 (s, J = 1.2 Hz, 1 H), 8.20 (extremely broad s, 5H), 4.22 (s, 3H), 1.7-0.1 (complex multiplet, 12H)). ^{13}C NMR (100.624 MHz, DMSO-d6 center peak = 39.51) δ 144.04, 131.53, 126.87 (N-Me peak not resolvable within the DMSO-d6 heptet). FTIR (HATR Method; significant peaks) 3546, 3318, 3224, 3109, 3032, 2460, 1748, 1732, 1622, 1564, 1524, 1475, 1434, 1401, 1364, 1324, 1238, 1209, 1062, 1038, 980, 948, 907, 874, 809, 715, 682, 618 cm.$^{-1}$

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5. Crystal data for C$_2$H$_{17}$B$_{12}$KN$_4$ (**1**): M_r=266.02, orthorhombic, space group *Pna2*(1), a=12.166(2), b=11.443(2), c=9.868(2)Å, α,β,γ=90°, V=1373.6(4) Å^3, F-(000)=544, ρ_{calcd}=1.286 gcm^{-3}, Z=4, μ=0.361 mm^{-1}, crystal size 0.3 x 0.2 x 0.2 mm^3, θ range 2.44 to 28.34, index ranges -16≤h≤16, -15≤k≤15, -13≤l≤13, Mo$_{K\alpha}$ (λ=0.71073 Å), T=296(2) K, 296. The single-crystal X-ray diffraction data were collected on a Bruker 3-circle-platform diffractometer equipped with a SMART APEX 2 detector with the χ-axis fixed at 54.74° and using MoK$_\alpha$ radiation from a fine-focus tube. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. The data collection as well as structure solution and refinement were carried out using standard procedures with the APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, and SHELXTL software packages and programs Bruker-AXS, INC.: Madison, WI USA, 2007. 29305 measured data of which 3418 (R_{int}=0.0231) unique. Transmission factors min/max 0.641/0.746, final *R* indices [I>2$\sigma(I)$]: R1=0.0231, wR2=0.0624, R indices (all data): R1=0.0246, wR2=0.0613, GOF on F^2=1.052. CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

6. The sluggishness in removal of the acetonitrile for many examples of the borane and carborane salts suggests some sort of significant borane-solvent interaction.

7. The term "binary" fits the carborane salts that stoichiometrically contain one heterocyclium cation paired with the carborane anion. For discussions in this report, the term binary also is extended to the borane salts that contain the **<u>same</u>** two heterocyclium cations paired with the borane di-anion. The term "ternary" is reserved for the mixed borane salts where two **<u>different</u>** heterocyclium cations are stoichiometrally paired in a 1:1 ratio with the borane di-anion. Similarly, salt (**12**) with a heterocyclium [Het]$^+$ cation and potassium [K]$^+$ cation stoichiometrically paired with the **same** borane di-anion is considered to be a "ternary" salt.

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9. Any attempt at recrystallizing the 1:1 mixture of cations in (**12**) is likely to afford enrichment in one or the other of the heterocyclium cations. The flash filtration, by virtue of eluting the two cations and the di-anion in electrostatic neutrality, preserves the 1:1 ratio to within experimental error of the NMR integration.

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11. Subsequent improved melting points of pure salts (**15**) and (**16**) were obtained from that originally determined for ref. 1.

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